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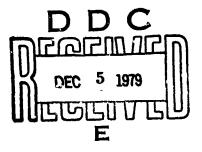
CORROSION LABORATORY



THE EFFECT OF PLASTIC DEFORMATION ON THE TRANSPORT OF HYDROGEN IN NICKEL

by

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Technical Report No. 3

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Office of Naval Research W. REPORT DATE Sep 800 Quincy Street Arlington, VA 22217 14. MONITORING AGENCY NAME & ADDRESS(II different from Controlling Office) 18. SECURITY CLASS. (of this report) 15a, DECLASSIFICATION/DOWNGRADING 16. CISTRIBUTION STATEMENT (of this Report) This document is unclassifed. Distribution and reproduction for any purpose of the US Government is permitted. 17. DIS' RIBUTION STATEMENT (of the abstract entered in Block 20, 12 different free Report) 18. SUPPLEMENTARY NOTES The attached is a preprint of a manuscript which is scheduled to appear in the Cctober 1979 issue of Scripta Metallurgica. 19. KEY WORDS (Continue on reverse side if necessary and identify by block number) hydrogen permeation, hydrogen embrittlement, nickel alloys, impurities ABSTRACT (Continue on reverse side if necessary and identify by block number)

The permeation of hydrogen into crystalline metals may occur in part by lattice diffusion, by grain boundary (or other short circuit) diffusion, or, in the case of specimens undergoing plastic deformation, by dislocation transport. In this work, electrochemical permeation measurements indicate that the apparent diffusivity of hydrogen is increased by several orders of magnitude when permeation specimens are plastically deformed and simultaneously charged with hydrogen.

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THE EFFECT OF PLASTIC DEFORMATION
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Introduction

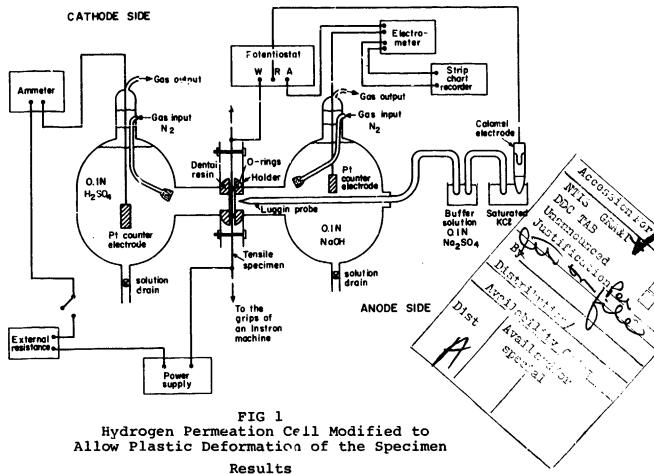
The permeation of hydrogen into crystalline materials may occur in part by lattice diffusion, by grain boundary (or other short circuit) diffusion, or, in the case of specimens undergoing plastic deformation, by dislocation transport (1). In the latter instance, the transport of hydrogen occurs in the form of Cottrell atmospheres dragged by mobile dislocations. This was first suggested by Bastien and Azou (2,3). Later, this concept has been supported by observations of serrated yielding (4-7), tritium release measurements during plastic deformation and autoradiographic techniques (8-10). Recently, Tien et al (11) and Johnson and Hirth (12) have proposed models for the transport of hydrogen as Cottrell atmospheres on dislocations and the generation of internal supersaturations of hydrogen, respectively.

The objective of this note is to report direct hydrogen permeation measurements during plastic deformation in nickel showing that mobile dislocations transport hydrogen at rates much higher than lattice diffusion and compare the observed rates with theoretical predictions of the models.

Experimental

Strips of Ni 270 (99.97 %Ni) were cold rolled to a thickness of 0.43mm. Tensile bars with a gage length of 5cm and reduced section width of 1.875cm were machined from these strips. The specimens were annealed under an argon atmosphere at 1000°C and then water quenched. For permeation studies, they were polished with emery papers and one side (anodic) was coated with a thin layer of palladium by electroless deposition from "Pallamerse" solution.

The permeation of hydrogen was studied by the method developed by Devanathan and Stachurski (13), modified to allow plastic deformation of the specimen during the introduction of hydrogen. FIG 1 shows a schematic of the apparatus. The specimen was mounted between the two compartments giving a 0.3cm² area of exposure (FIG 2). The specimen-cell assembly was positioned between the crossheads of an Instron machine. The anodic side was potentiostated at a potential above the reversible potential for the hydrogen electrode. Cathodic charging was performed galvanostatically. Specimens were deformed at a constant extension rate. An immediate increase in the background anodic current is observed at the onset of macroscopic plastic deformation, perhaps due to accelerated anodic dissolution in the presence of plastic deformation or to disruption of surface films. After some time, the current reaches a steady state value and at this point hydrogen charging is begun (FIG 3). Permeation currents and stress-strain curves were recorded. All experiments were run at room temperature.



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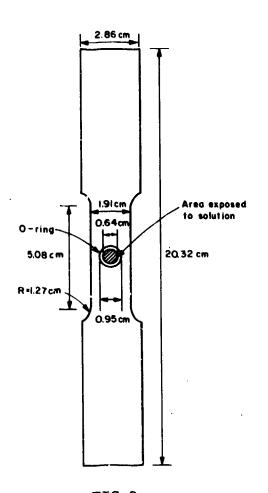
A typical permeation transient in unstrained nickel is shown in FIG 4. $D_{\rm H}$ is about $10^{-10}\,{\rm cm^2/s}$. Typical permeation build-up and decay transients under plastic deformation are shown in FIGS 5 and 6. Hydrogen permeates through the specimen in less than 10 seconds and a steady state is reached in less than a minute. On switching off the charging current, the anodic current decays to the value observed prior to charging (FIG 3). When deformation is stopped the anodic current decays back to the original background value. From FIGS 5 and 6, it can be seen that increasing strain rate increases the observed permeation flux. Increasing charging current also gave higher permeation fluxes. The largest strain rate (4.2 x $10^{-4}/{\rm s}$) was below the critical strain rate, given by $^{-10^{-11}}\rho_{\rm H}$ (11) ($\rho_{\rm H}$ = density of hydrogen-carrying dislocations), above which hydrogen transport does not occur. FIG 6 shows decay transients for two different strain rates (observed after switching off the charging current). In the case of the higher strain rate, the decay is much faster.

The mathematics of hydrogen permeation has been dealt with elsewhere (13-16). By applying Fick's second law with the appropriate initial and boundary conditions and using the half-rise time method, $D_{\rm H}$ can be evaluated. In plastically deformed nickel, the "effective" $D_{\rm H}$ was found to be of the order of $10^{-5} {\rm cm}^2/{\rm s}$ in contrast to $10^{-10} {\rm cm}^2/{\rm s}$ in unstrained nickel, the latter of which compares well with the findings of Robertson (17).

Discussion

From these results, it is evident that in plastically deformed nickel, dislocation transport of hydrogen is the predominant mechanism and that the transport rates are several orders of magnitude higher than in unstrained nickel where

lattice diffusion is probably the predominant mechanism.



E100 /NW) *** **= 50** Strain (%) 1.8 Start Charging Stop Charaina Stop Deformation 1.5 1.2 PERMEATION 0.9 Accelerated corresion or disruption of 0.6 surface films due to plastic deformation 0.3 15 25 30 5 Time (min)

FIG 2 Specimen for Permeation Experiment Designed to Allow Plastic Deformation During Polarization

FIG 3
Correlation Between Permeation Current and
Plastic Deformation

Increasing strain rate leads to higher permeation fluxes. This is due to higher average dislocation velocities and a higher dislocation density as given by the relationship

$$\dot{\varepsilon} = \rho h v \tag{1}$$

where $\dot{\epsilon}$ is the strain rate, ρ is the density of mobile dislocations, v is the dislocation velocity and b the Burgers vector.

The difference in the decay transients (FIG 6) can also be considered in terms of dislocation velocities. In the case of the higher strain rate, the average dislocation velocity is larger and thus hydrogen is drained out of the specimen faster on switching off the charging current.

Increasing charging currents lead to higher permeation fluxes due to the higher concentration of hydrogen introduced into the specimen.

Tien et al (11) have proposed a quantitative model for hydrogen transport by mobile dislocations. They derived the following expression for the maximum penetration distance of hydrogen in plastically deformed metal

$$x_1 = \frac{D_H}{kT} \frac{E_B}{3Cb} t_p \tag{2}$$

where Ep is binding energy of hydrogen to dislocation, 30b is interaction distance of the dislocation with the impurity cloud, $D_{\rm H}$ is diffusion coefficient

of hydrogen and tp is duration of plastic deformation.

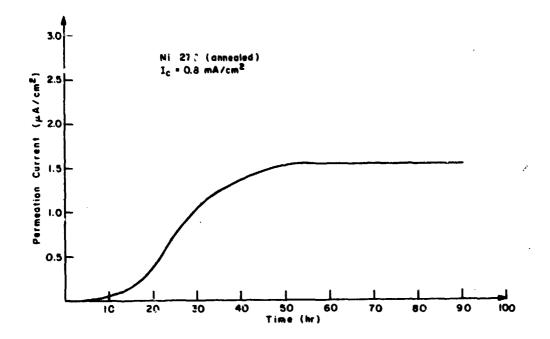


FIG 4
Permeation Transient in Unstrained
Nickel

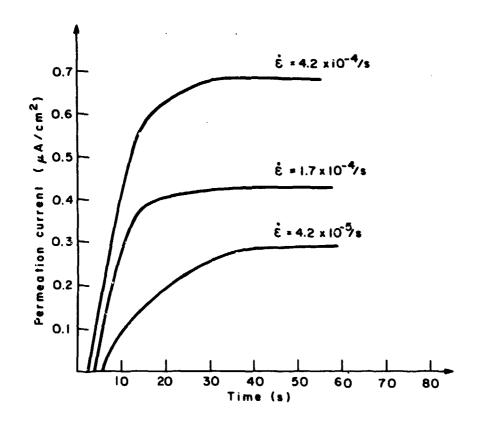


FIG 5
Effect of Strain
Rate on Permeation
Behavior
(I_C = 50mA)

In contrast, the penetration distance due to the lattice diffusion is $x_2 = 4\sqrt{D_H t_p} \tag{3}$ Applying these two equations to the present case, we obtain the following

expression for the ratio x_1/x_2 $\frac{x_1}{x_2} = 10^2/\overline{t_p}$

$$\frac{\mathbf{x}_1}{\mathbf{x}_2} = 10^2 \sqrt{\mathbf{t}_p} \tag{4}$$

Using equations (3) and (4) one finds that about five seconds of plastic deformation are required for hydrogen to travel through specimens of thickness used in this study. This calculation shows that the model by Tien et al is in good agreement with the observed transport rates.

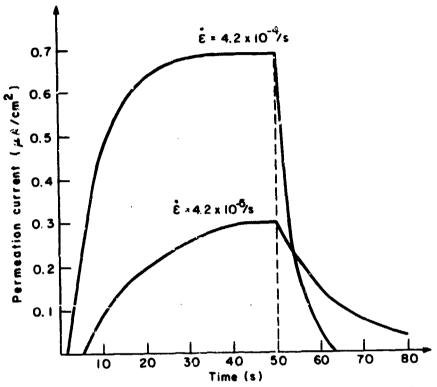


FIG 6
Effect of Strain Rate
on the Decay Transient
(I_C = 50mA).

Effect of Strain Rate on the Decay Transient I_c $\pm 50 \text{mA}$

Conclusions

It has been shown that mobile dislocations in nickel transport hydrogen at rates far in excess of lattice diffusion. Increasing strain rate and charging current increase the permeation flux of hydrogen. The observed transport rates agree with the predictions of the model by Tien et al.

Acknowledgements

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